

Problem Set #3

1) Construct a MO diagram for the hypothetical molecule $\text{Mo}_2\text{H}_8^{4-}$. Use the 1s orbitals on the 8H atoms and the d orbitals on each Mo^{2+} . Indicate the symmetry of each orbital, and whether it has metal-metal and metal-hydrogen character.

2) Use the energy level diagram for ferrocene on p 245 of your text to predict the lowest vibronically allowed electronic transition or transitions if several are expected to be close in energy. What is the lowest dipole allowed electronic transition? Give both the orbital transition and state symmetries. Indicate the polarization expected for the dipole allowed transition.

3) Would you expect the ferrocenium cation (obtained on one-electron oxidation) to have the identical symmetry structure as ferrocene.

4) The Tanabe Sugano diagrams on p 276-277 of your text show how the electronic states for octahedral complexes vary with increasing strength of the ligand field. What is the significance of the vertical line in the figures for the d^4 , d^5 , d^6 , and d^7 cases? What would you expect to be the lowest spin-allowed, but dipole forbidden d-d transitions in $\text{Co}(\text{H}_2\text{O})_6^{2+}$ and in $\text{Co}(\text{CN})_6^{4-}$. Hint: review the spectrochemical series for ligands.

5) Do problem 9.5 in your text.

6) Show that the four operations given by the four equivalent positions in the $P2_1/c$ space group satisfy the requirements for a group.

7) The general formula for the volume of a unit cell is given by:

$$V = abc \sqrt{(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma) + 2\cos\alpha \cos\beta \cos\gamma}$$

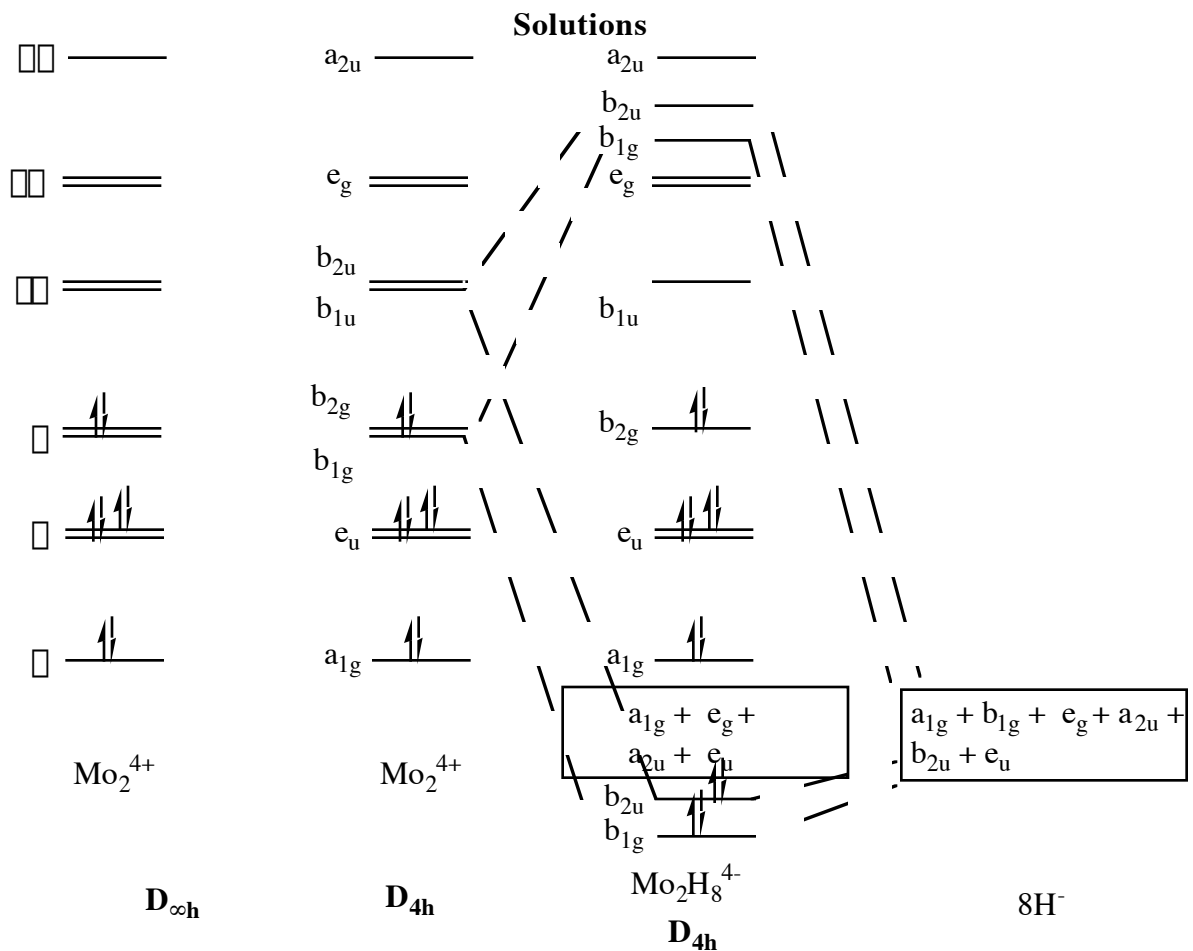
A crystal of $[\text{Cu}_2(\text{tren})_2(\text{CN})_2](\text{BPh}_4)_2$ has a density of 1.27 g/cm^3 and crystallizes in the monoclinic unit cell $P2_1/c$ with $a = 13.792 \text{ \AA}$, $b = 10.338 \text{ \AA}$, $c = 20.316 \text{ \AA}$, and $\beta = 94.27^\circ$. (tren = tris-2-aminoethylamine $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$). What is the number of molecules in the unit cell? Is there any symmetry required of the dimeric compound?

8) Do problem 11.4 in your text.

9) Do problem 11.5 in your text.

10) Do problem 11.7 in your text.

11) Do problem 11.9 in your text.



As shown in class for $\text{Re}_2\text{Cl}_8^{2-}$, the dinuclear metal orbitals can be classified as in a diatomic on the left side. These correlate in the D_{4h} symmetry of the dimer as shown. The symmetry representations of the 8H^- ligands transform in D_{4h} as:

$$\chi(\text{H}_{\square}) = \begin{matrix} E & 2C_4 & C_2 & 2C_2' & 2C_2'' & i & 2S_4 & \sigma_h & 2\sigma_v & 2\sigma_d \\ \hline 8 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 4 & 0 \end{matrix} = a_{1g} + b_{1g} + e_g + a_{2u} + b_{2u} + e_u$$

Only the $d_{x^2-y^2}$ orbitals derived from the $\square(b_{1g})$ and $\square(b_{2u})$ combinations point at the H^- orbitals and that interaction is shown.

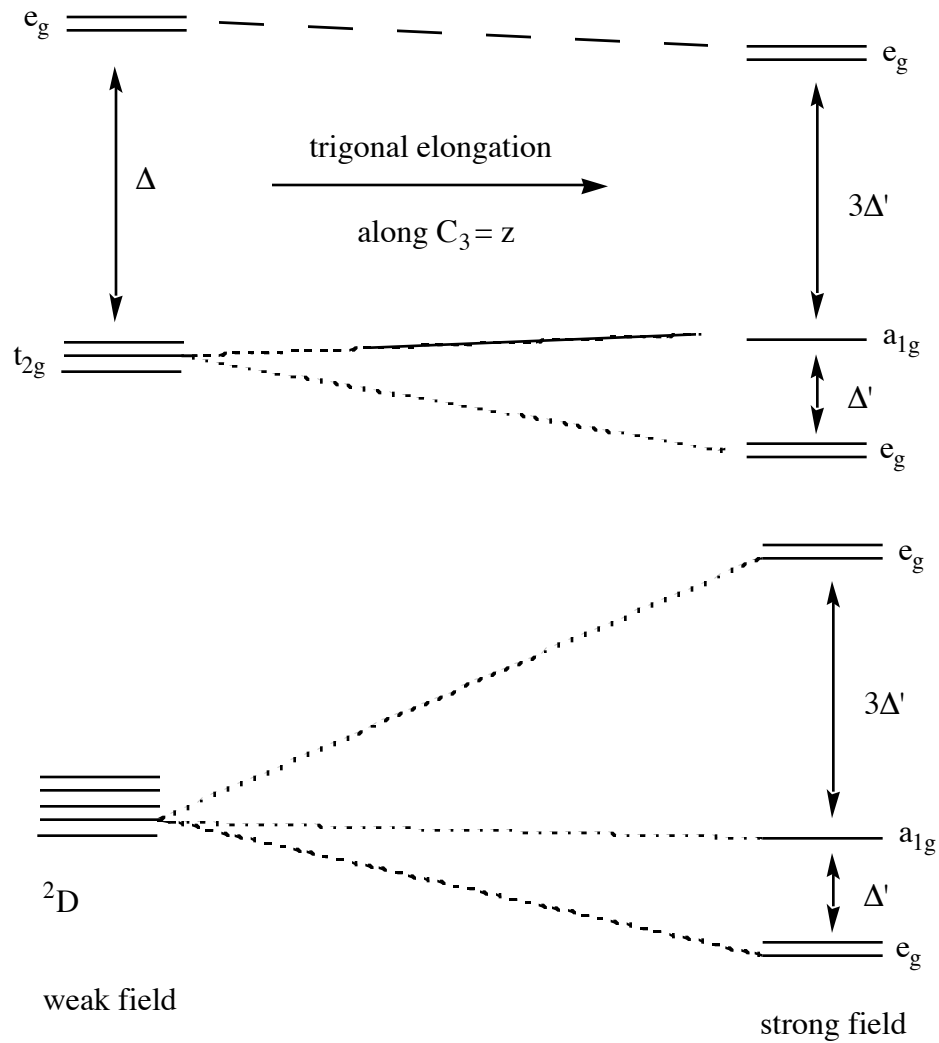
2) The lowest one electron transition is $e_{2g} \rightarrow a_{1g}$. This $e_{2g}^3 a_{1g}^1$ configuration will generate the ${}^1E_{2g}$ excited state. This is dipole forbidden, as the ground state is ${}^1A_{1g}$, but will be vibronically allowed by coupling with a vibration of symmetry such that the direct product $E_{2g} \cdot \text{vib} \cdot a_{2u}$ or $E_{2g} \cdot \text{vib} \cdot e_{1u}$ contains the totally symmetric representation. This will occur for vibrations of e_{2u} and e_{1u} symmetry. The skeletal vibrations of ferrocene include two e_{1u} vibrations corresponding to a ring tilt and a metal-ring slip (p391 of Nakamoto).

Thus, this transition is vibronically allowed. The next promotion $e_{2g} \rightarrow a_{2u}$, gives rise to the excited singlet state ${}^1E_{2u}$. This is not dipole allowed either. The next $e_{2g} \rightarrow e_{1u}$ promotion yields ${}^1E_{2u}$ and ${}^1E_{1u}$ states. The transition ${}^1A_{1g} \rightarrow {}^1E_{1u}$ is dipole allowed with x,y polarization.

3) The ferrocenium cation has a hole in the e_{2g} orbital, which would yield a ${}^2E_{2g}$ ground state. This is forbidden by the Jahn-Teller distortion and should distort from D_{5d} symmetry along the a_{2g} or e_{1g} normal modes. The e_{1g} ring tilt is one possibility.

4) The vertical lines in the T-S diagrams correspond to a change in the ground state from a high spin to a low spin configuration as the crystal field strength increases. In the d^7 cobalt complexes, the lowest spin-allowed and dipole-forbidden electronic transition in the high spin aquo complex is ${}^4T_{1g}(t_{2g}^5e_g^2) \rightarrow {}^4T_{2g}(t_{2g}^4e_g^3)$. In the strong-field cyanide complex, it would be ${}^2E_g(t_{2g}^6e^1) \rightarrow {}^2T_{1g}$ according to the diagrams in your text. (note: the diagrams omit the g/u subscripts, since they also apply to tetrahedral complexes - d^3 octahedral and d^7 tetrahedral have the same diagrams, thus you must add the subscript g to the d orbital states in the octahedral case.)

5) For a d^1 case:



The d^2 case (the problem in the text isn't specific) is more complicated, but can be simply obtained from Fig 9.3 by splitting the free ion states according to Table 9.3 (using the D_3 entries and adding a sub g for the D_{3d} representations) and correlating with the strong field states (e_g^2 , $e_g^1 a_{1g}^1$, a_{1g}^2 , $a_{1g}^1 e_g^1$, and e_g^2). For the singly occupied orbitals the state symmetries are given by the direct products, $a_{1g}^2 = ^1A_{1g}$, and for e_g^2 you must use the symmetric direct products.

6) The four operations in $P2_1/c$ are:

$$E = (x, y, z)$$

$$2_1 = (-x, y + 1/2, -z + 1/2)$$

$$i = (-x, -y, -z)$$

$$c \text{ glide} = (x, -y + 1/2, z + 1/2)$$

First show closure:

$$\text{e.g. } i 2_1(x, y, z) = i(-x, y+1/2, -z+1/2) = (x, -y-1/2, z-1/2)$$

Now we can add a unit translation along y and z, because of the periodic symmetry to yield

$$(x, -y+1/2, z+1/2), \text{ which is the } c \text{ glide. Thus, } i 2_1 = c \text{ glide.}$$

Similarly $i c = 2_1$, $c c = E$, $2_1 2_1 = E$, $i i = E$ and

$$2_1 i(x, y, z) = 2_1(-x, -y, -z) = (x, -y+1/2, z+1/2) = c$$

$$c i(x, y, z) = (-x, y+1/2, -z+1/2) = 2_1$$

$$2_1 c(x, y, z) = 2_1(x, -y+1/2, z+1/2) = (-x, -y+1, -z) = (-x, -y, -z) = i$$

$$c 2_1(x, y, z) = c(-x, y+1/2, -z+1/2) = (-x, -y, -z+1) = i$$

The other properties of the identity, and inverse have already been shown and the associative character follows from the summarized multiplication table.

	E	2_1	i	c
E	E	2_1	i	c
2_1	2_1	E	c	i
i	i	c	E	2_1
c	c	i	2_1	E

$$7) \quad V = abc \sqrt{(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma - c^2 \sin^2\alpha - 2\cos\alpha \cos\beta \cos\gamma)} = (13.792\text{\AA})(10.338\text{\AA})(20.316)\text{SQRT}((1 - \cos^2 94.27^\circ)) = 2889 \text{\AA}^3 = 2889 \times 10^{-24} \text{cm}^3$$

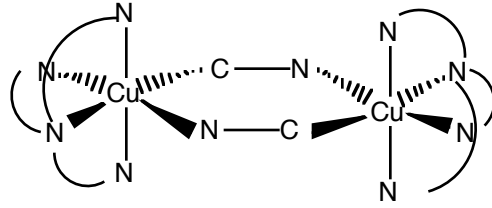
Now experimentally 1.27 g/cm^3 is the density.

The molecular formula is $[\text{Cu}_2(\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3)_2(\text{CN})_2][\text{B}(\text{C}_6\text{H}_5)_4]_2 =$

$$\text{Cu}_2\text{N}_{10}\text{B}_2\text{C}_{62}\text{H}_{76} = 1110 \text{ g/mole} = 1.84 \times 10^{-21} \text{ g/molec}$$

If there were one molecule in the unit cell, then there would be

$1.84 \times 10^{-21} \text{ g/molec} / 2889 \times 10^{-24} \text{ cm}^3 = 0.636 \text{ g/cm}^3$ if there were only one molecule of the dimer per unit cell. The experimental density is about twice this, which implies there must be two molecules in the unit cell volume. In the space group $P2_1/c$ there are four general positions, so if the dimer comprises an asymmetric unit it must be on one of the special positions. This is because there are only two asymmetric units required for the special positions. Although there are four different pairs of special positions, all are required to possess inversion symmetry. Therefore the dimer must have inversion symmetry, which would be consistent with the following geometry about the copper atoms.



8) Applying a glide plane twice (reflect twice and translate by $2(1/2)$) brings is equivalent to translation by 1 unit cell length. If the glide plane involved any other fraction, say $1/3$, then applying it twice would yield translation by $2/3$ of the unit cell length, which is not a translational symmetry element. If this were possible, then the true unit cell length along this direction would be $2/3$ of the repeat unit.

9) The triclinic lattice (p 390) has 8 inversion centers at $(0,0,0)$, $(1/2,0,0)$, $(0, 1/2,0)$, $(0,0,1/2)$, $(1/2,1/2,0)$, $(1/2, 0, 1/2)$, $(0, 1/2, 1/2)$, and $(1/2, 1/2, 1/2)$.

10) The space group $Pna2$ would have the symmetry operations:

- x,y,z identity
- $-x,-y,z$ twofold
- $-x, y+1/2, z+1/2$ n-glide
- $x + 1/2, -y + 1/2, z$ a-glide

twofold times n-glide = $x,-y +1/2, z+1/2$ = a c-glide perpendicular to b with a translation $1/2$ along b. This means the b axis is half that assumed. The two fold times the a glide would = $-x+1/2, y+1/2, z$, which is a b glide perpendicular to a at $a=1/4$. This means that a is also $1/2$ that assumed. The n glide time a-glide = $-x + 1/2, -y, z + 1/2$, which is 2_1 along b, which is a consequence of the doubled repeat along b. If we remove the $1/2$ translation along b, by making the new b axis $1/2$ what it was, then the n glide becomes a c glide. Thus, the new group with the b axis halved is $Pba2$.

11) From Table 11.4, isometric, trigonal, tetragonal, orthorhombic, monoclinic, orthorhombic, tetragonal, orthorhombic.